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(54) Cement colouring composition

(57) The composition is a thixotropic slurry which comprises: (a) 20 to 70 wt.% of a solid particulate pigment which may have particle sizes in the range 0.5 to 40 microns; (b) 0.4 to 15 wt.% of a stabilizer; (c) 0.1 to 3 wt.% of a dispersant; (d) 12 to 77 wt.% of an aqueous carrier containing 5 to 35 wt.% of a freezing point depressant, so that the slurry freezes only below —5°C, preferably only below —10°C.

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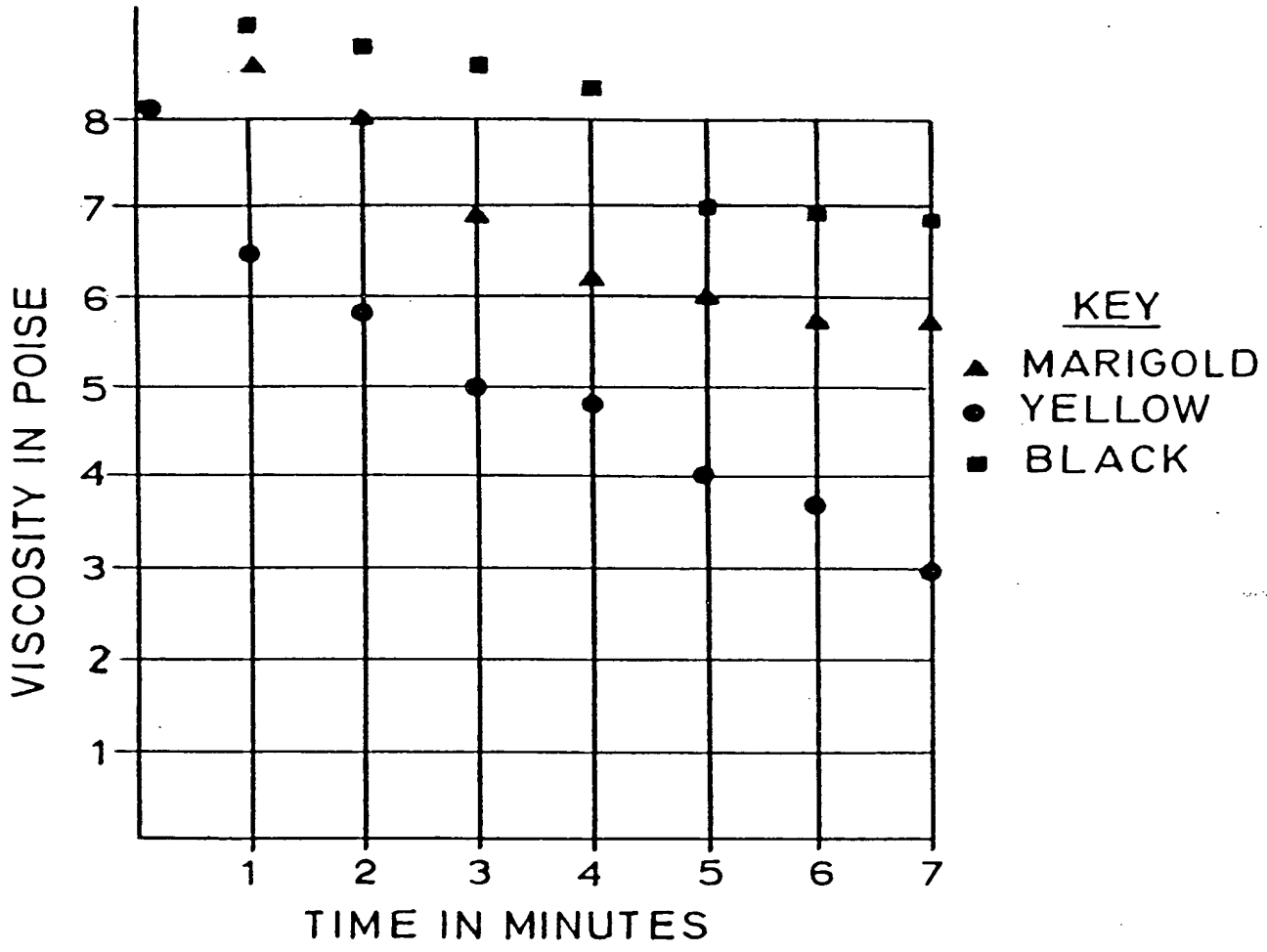
VISCOSITY IN POISE
1
2
3
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6
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TIME IN MINUTES
1
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3
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6
7
KEY
MARIGOLD
YELLOW
BLACK

SPECIFICATION

Cement colouring composition

This invention relates to a colouring material for cementitious mixes used in making products such as cast concrete, extruded concrete, cement fibre glass, and cement asbestos.

Conventional cement or concrete colouring compositions comprise powders which are added by hand or by a screw conveyor in their dry state to a wet concrete or cement mix in a mixing apparatus. It is difficult to accurately add desired amounts of such powders to the wet concrete mix and there is often waste of such colouring material. Furthermore, with powders it is difficult to obtain a sufficiently thorough mixing of the powders into the wet cement mix so as to achieve a homogeneous colour throughout the mixture. Conventional methods also require the concrete or cement contractor to maintain large inventories of the colouring composition and involve certain health hazards as well.

It is highly desirable to have a system for colouring wet cement and concrete mixes by the addition of the colouring material in a liquid form to the mix, so that the colouring material may be added by liquid pumps to the wet concrete mix. In particular it is desirable to be able to supply a pigment suspension which will not settle out within a relatively short time.

The present invention provides a colouring composition for a cementitious mix, the composition being a thixotropic slurry comprising: a solid particulate pigment; a stabilizer; a dispersant; and an aqueous carrier containing a freezing point depressant in such an amount that the slurry freezes only below −5°C, preferably only below −10°C.

The preferred composition comprises: pigment, 20 to 70 wt.%, stabilizer, 0.4 to 15 wt.%; dispersant, 0.1 to 3 wt.%; aqueous carrier, 12 to 77 wt.%. The amount of freezing point depressant is preferably 5 to 35% based on the weight of the aqueous carrier.

It has been found that without the freezing point depressant the storage life of the slurry is sometimes shorter than expected. It is believed that this is owing to the effect of low temperatures when storage extends into the winter. The inclusion of the freezing point depressant brings an improvement in storage life which appears to be due not only to the lower freezing point but also to the fact that, if the slurry does freeze, the way in which it freezes (passing through a paste-like state) inhibits settling out.

The invention will be described further, by way of example, with reference to the accompanying drawing, whose sole Figure is a graph illustrating preferred ranges of viscosity plotted against time for three exemplary iron oxide pigments after they have been processed into slurries by the general method shown in Figure 1.

In the following description all percentages are by weight.

EXAMPLE 1

A mixing tank having a slow speed or low energy agitator revolving at 80 to 200 rev/min is partially filled with 47.17% (based on the weight of slurry to be produced) of an aqueous carrier consisting of an aqueous solution of ethylene glycol (10% solution). A natural gum such as gum arabic in the amount of 5% is then added as well as 0.66% of a dispersant such as sodium laurate, which is a sodium salt of lauric acid sulphonate. At ambient temperatures, the water, the dispersant and stabilizer are premixed until all are dissolved. Then, while the mixer is still running, 47.17% of a pigment such as black iron oxide is added and the entire mixture is then mixed for about one hour, for example, until it is uniform and homogeneous whereupon it will have a predetermined specific gravity.

Next, the material is pumped into a high speed or high energy mill such as a stone mill, for example, to reduce the particle size of the pigment component of the slurry down into the micron range. This can be checked by the use of a grinding "wedge" or other gauge. Preferably, the pigment particle size distribution in the resulting thixotropic slurry should include largest particles with a maximum dimension of about 40 microns, large particles whose average size is about 25 microns, smaller particles whose average size is in the 1—2 micron range, and smallest particles down to a minimum size of about 0.5 microns. If the particle distribution is generally higher than these ranges, the colouring strength of the slurry is adversely affected. If the sizes of the particles are generally below these ranges they may be washed out of dried concrete by normal weathering.

The slurry froze below −15°C.

The procedure described above may also be applied to many other formulations such as are set forth in the following examples:

EXAMPLE 2

Black Iron Oxide	47.17%
Aqueous carrier	47.73%
Gum Arabic	5.00%
Sodium Laurate	0.10%

EXAMPLE 3

Carbon Black	20.00%
Aqueous carrier	76.60%
Gum Arabic	0.4%
Ethylene Oxide Condensate	3.0%

EXAMPLE 4

Carbon Black	25.0%
Aqueous carrier	59.0%
Alginate L.V.	15.0%
Sodium Laurate	1.0%

EXAMPLE 5

Spanish Red Oxide	80.0%
Aqueous carrier	12.69%
Gum Arabic	7.0%
Ethylene Oxide Condensate	0.4%

EXAMPLE 6

Red Oxide (Natural)	60.00%
Aqueous carrier	30.00%
Gum Arabic	9.20%
Sodium Laurate	0.80%

EXAMPLE 7

Red Oxide (Synthetic)	50.00%
Aqueous carrier	47.00%
Gum Arabic	2.80%
Sodium Laurate	0.20%

EXAMPLE 8

Yellow Oxide (Synthetic)	47.00%
Aqueous carrier	49.5%
Gum Arabic	3.2%
Sodium Laurate	0.3%

EXAMPLE 9

Yellow Oxide (Synthetic)	47.00%
Aqueous carrier	49.5%
Sodium Alginate (Manute RS)	3.2%
Sodium Laurate	0.3%

EXAMPLE 10

Yellow Oxide (Synthetic)	47.00%
Aqueous carrier	49.5%
Carboxymethyl Cellulose (CMC) High Viscosity grade	3.2%
Sodium Laurate	0.3%

EXAMPLE 11

Yellow Oxide (Synthetic)	47.00%
Aqueous carrier	49.5%
Gum Arabic	3.4%
Triethanolamine	0.1%

EXAMPLE 12

Yellow Oxide (Synthetic)	47.00%
Aqueous carrier	49.5%
Gum Guar	3.2%
Sodium Laurate	0.3%

EXAMPLE 13

Yellow Oxide (Synthetic)	47.00%
Aqueous carrier	49.5%
Gum Tragacanth	3.2%
Sodium Laurate	0.3%

EXAMPLE 14

Yellow Oxide (Synthetic)	47.00%
Aqueous carrier	49.5%
Locust Bean Gum	3.2%
Sodium Laurate	0.3%

EXAMPLE 15

Yellow Oxide (Synthetic)	47.00%
Aqueous carrier	49.5%
Dextrine	3.2%
Sodium Laurate	0.3%

EXAMPLE 16

Yellow Oxide (Synthetic)	47.00%
Aqueous carrier	49.5%
Potato Starch	3.2%
Sodium Laurate	0.3%

EXAMPLE 17

Yellow Oxide (Synthetic)	47.00%
Aqueous carrier	49.5%
Polyvinyl Alcohol	3.2%
Sodium Laurate	0.3%

EXAMPLE 18

Yellow Oxide (Synthetic)	47.00%
Aqueous carrier	49.5%
Polyvinyl Alcohol	3.2%
Sodium Laurate	0.3%

The dispersant help the slurry to keep its suspended state for long periods of time, and they facilitate the incorporation of large amounts of pigment into the slurry. They also tend to prevent flocculation of the pigment when the slurry is added to a cement mix containing free calcium ions. Less flocculation makes for more intense colouring of the cement mix.

In each of the above examples the aqueous carrier consists of an aqueous solution of a freezing point depressant in such an amount that the slurry freezes only below a given sub-zero temperature. By way of example, in order to achieve a freezing point of −25°C, any one of the following freezing point depressants can be used in the following percentages based on the quantity of aqueous solution: magnesium sulphate 25%; sodium sulphate 25%; ethylene glycol 15%; propylene glycol 17%; glycerol 20%; sorbitol 20%; ethyl alcohol 30%; methyl alcohol 33%; isopropyl alcohol 33%. Magnesium and sodium sulphate have a slight retarding effect on the curing of the cementitious products. The alcohols appear not to affect curing, even when used at high concentrations, e.g. 8 to 10% based on the weight of the cementitious mix.

It is important that the viscosity of the formulation be controlled so as to ensure that the formulation can be fluidized when being dispensed, thereby to optimize the mixing of the formulation with the cement or concrete components. The product is therefore checked as to its viscosity, which should fall substantially within the limits (measured in poise) as shown in the accompanying drawing. While the data shown in the graph just deals with iron oxides, the desirable viscosity ranges for other pigments will also fall within the maximum and minimum ranges shown in that drawing. The data plotted was determined by the use of a "Rotothinner" brand viscometer manufactured by ICI. This viscometer works by detecting mechanical shear, not by the detection of heat generation.

The colour quality of the slurry may be tested by adding to it a predetermined quantity of titanium dioxide (white) in the 3:1 to 5:1 ratio range. This measures the relative value of the

colour, since a given sample may require a different amount of the colouring pigment to produce the same tint as another batch of the slurry.

Other usable stabilizers include active clays such as bentonite, kieselgur, or benagel, uncooked corn or wheat starch, water-soluble celluloses such as hydroxy ethyl cellulose or methyl cellulose, and polyvinyl pyrolidone.

Other usable dispersants include other fatty amines and alkylamines. Cationic surfactants, such as "Wetfix SE" (trade mark), are particularly suitable for compositions to be used for colouring cement asbestos.

Optionally, other substances may also be added to impart desired characteristics to the composition. For example, a small percentage, say 4 to 7% of an anti-efflorescent agent such as barium carbonate can be added. Or small percentages (say about 2%) of water-repellent chemicals such as calcium stearate, aluminium stearate, or silicones can be added to the pre-mix of the dispersant and the stabilizer in the aqueous carrier.

The premixing step may be alternatively accomplished by using a hydraulic, variable speed cavitation mixer such as those marketed by Torrance & Sons of Bristol, England or by Cowles in the United States. Present cavitation mixers are, however, somewhat limited in processing capacity.

The reduction of the particle size of the original slurry by high energy processing may be done by mills other than the stone mill. Alternatively, a Premier brand colloid mill manufactured by Premier Colloid Mills or other types of comminuting apparatus may be employed. Stone mills may be those manufactured by Moorhouse in the United States or by Fryma in Switzerland. Ball mills or rod mills have also been satisfactorily used, but they have the disadvantage of requiring more processing time. Attrition mills such as sand mills or pearl mills also are effective, but also usually take longer than high speed mills or colloid mills.

One of the main advantages of the present invention is that thixotropic slurries of various main colours may be packaged in drums or other containers and the suspensions will not settle out for relatively long periods of time, i.e. of the order of 6 to 12 months. Thus, if the concrete or cement contractor wishes, he can keep perhaps 3 to 5 pigment slurries in individual drums, each slurry being operatively connected to a batching system which controls the amounts of the slurries to be added to the concrete mix. A charging pump may be inserted into each drum of slurry connected through a delivery tube to a metering container or tube. The tube may for example, contain a first (higher) measuring probe connected to a batching control unit whose height is adjustable (or predetermined) depending upon the amount of slurry to be measured out. Operation of the charging pump delivers the slurry to the metering tube until it touches the lower end of the first measuring probe whereupon a circuit is actuated which cuts off the pump. The charging pump for applying the slurry to the metering tube may be an air-operated positive displacement piston pump such as those marketed by Graco, Inc. of Minneapolis, Minnesota. Then the contents of the metering tube start to be withdrawn from the metering tube by the action of a dispensing pump (controlled by the batching unit) and to be applied (with water) to a concrete mixer of any conventional type. When the level of the metered slurry falls below the lower end of a second probe coupled to the batching unit, a signal is generated which stops the dispensing pump.

If the contents of the slurry drum have not been used for excessive lengths of time, it may be advisable to insert a recycling valve branching off from the output of the charging pump and being connected to a recycling tube which returns to the drum. The return of the slurry back to the drum will produce a certain amount of agitation of the contents of the drum.

Instead of the batching system described above, it is also possible to use a positive displacement pump of the said Graco type or of the "Mono" brand type marketed by Mono Pumps Ltd. of Great Britain. The latter pump is also marketed in the United States under the "Moyno" brand by Robbins and Meyers. The pump is set to run for a timed period so that, since the rate of flow is known, the amount of pumping time required to produce a given volume can easily be calculated. The timers may be wired to the electric motor starters of the pumps.

Still another method is to pump the slurry around a continuous circuit *via* a three-way valve which is air or electrically operated. The valve is connected to a timer that can switch it from continuous circuit to injection by-pass, either straight into the mixing apparatus or indirectly, *via* a weighing scale, into the mixer so as to provide a double check on the quantity required for addition.

CLAIMS

1. A colouring composition for a cementitious mix the composition being a thixotropic slurry, comprising:
   (a) a solid particulate pigment,
   (b) a stabilizer,
   (c) a dispersant, and
   (d) an aqueous carrier containing a freezing point depressant in such an amount that the slurry freezes only below −5°C.

2. A composition as claimed in claim 1, comprising:
   (a) 20 to 70% by weight of the solid particulate pigment,
   (b) 0.4 to 15% by weight of the stabilizer,
   (c) 0.1 to 3% by weight of the dispersant, and
   (d) 12 to 77% by weight of the aqueous carrier.

3. A composition as claimed in claim 1 or 2, in which the pigment comprises at least one of the following: metallic oxides, metallic salts, and carbon black.

4. A composition as claimed in any of claims 1

to 3, in which the pigment particle sizes are substantially within the range 0.5 to 40 microns.

5. A composition as claimed in any of claims 1 to 4, in which the stabilizer comprises at least one of the following: active clays, natural products of the alginate group, hydrolysed starches, water-soluble celluloses, natural starches, synthetic polymers of the polyvinyl type, and water-soluble natural gums.

6. A composition as claimed in any of claims 1 to 5, in which the dispersant comprises at least one of the following: ethylene oxide condensates, fatty amines, alkylamines, and sulfonated soaps in the form of a metal derivative salt.

7. A composition as claimed in any of claims 1 to 5, for colouring cement asbestos, in which the dispersant is a cationic surfactant.

8. A composition as claimed in any of claims 1 to 7, in which the amount of freezing point dispersant is such that the slurry freezes only below −10°C.

9. A composition as claimed in any of claims 1 to 8, in which the aqueous carrier contains 5 to 35% by weight of the freezing point depressant.

10. A composition as claimed in any of claims 1 to 9, in which the freezing point depressant comprises an alcohol.

11. A method of colouring a cementitious mix, in which a colouring composition according to any preceding claim is incorporated into the mix.

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